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PATENT SPECIFICATION

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(54) METAL-HALOGEN ELECTROCHEMICAL CELL

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

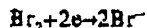
This invention relates to metal-halogen electrochemical cells having an aqueous solution of a metal halide as the electrolyte. In particular, the present invention relates to improved electrochemical cells, including batteries, employing a zinc or cadmium anode, a bromine cathode and an aqueous metal bromide electrolyte in which the metal is the same as the metal of the anode.

Cells for the production of electricity having two electrodes, one with a high positive oxidizing potential, the anode, and one with a strong negative or reducing potential, the cathode, have long been known. Typical of such type cells as metal-halogen cells in which the anode material most commonly employed is zinc and the most commonly employed cathodic halogen is bromine. Among the advantages of such cells is their extremely high theoretical energy density. For example, in the zinc-bromine cell, the battery will have a theoretical energy density of 200 Wh/lb. (i.e., watt hours per pound) and an electric potential of about 1.85 volts per cell.

In such a cell the surface of the anode, for example, zinc, oxidizes, i.e., undergoes a positive increase in valence. As a result thereof, zinc atoms are converted to zinc ions which enter the electrolyte according to the equation:



The chemical reaction occurring at the cathode is expressed by the following equation:

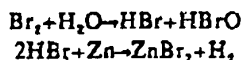


Thus, the overall chemical reaction can be written as follows:



The arrow to the right indicates the direction of the chemical reaction occurring during cell discharge and the arrow to the left indicates the chemical reaction occurring during charging of the cell.

The electrochemical cells of the foregoing type are known to suffer from a number of disadvantages. Most of these disadvantages are associated with side reactions which may occur in such cells. For example, during the charging process free bromine is produced in the cell. This free bromine is available for chemical reaction with the metal anode, e.g., zinc, thereby resulting in an autodischarge of the cell. Additionally, there is the tendency for hydrogen gas to be generated when considerable amounts of free bromine are present in the aqueous phase. It is believed that hydrogen is generated according to the following chemical reactions:



The art is replete with efforts on the part of many inventors to overcome the above-mentioned disadvantages. U.S. Patent 2,566,114, for example, discloses the use of tetraethyl and tetramethyl ammonium bromides for binding bromine generated during charging of the cell. The tetraalkyl ammonium bromide is added to the powdered carbon surrounding the cathode.

U.S. Patent 3,738,870 discloses the use of the solid mixture of an alkyl ammonium perchlorate and conductive materials such as graphite to form solid addition products with halogen released during charging of such cells.

U.S. Patent 3,811,945 discloses the use of certain alkyl ammonium perchlorates, diamine bromides and diamine perchlorates, which are capable of forming solid addition products with cathodic bromine and which are substantially insoluble in water.

In contrast to those references which suggest forming solid addition products with bromine, U.S. Patent 3,408,232 discloses the use of an organic solvent for elemental bromine in such aqueous zinc-bromine batteries.

U.S. Patent 3,816,177 discloses the use of a quaternary ammonium halide and a depolarizer in the electrolyte. The depolarizer is an organic complexing solvent which dissolves in water and is nonreactive towards the halogen in the cell and forms a water insoluble complex in the presence of quaternary ammonium halides.

These references and many others show a continuing effort on the part of many inventors to overcome some of the disadvantages associated with the metal halogen cells of the type referred to herein. Unfortunately, the methods proposed for overcoming the aforementioned disadvantages have not adequately overcome such disadvantages. There is, consequently, a need for more effective methods for preventing loss of cell capacity in aqueous zinc-halogen cells.

The present invention is predicated on the discovery that molecular bromine is sufficiently separated from an aqueous solution in the form of a liquid complex by chemical reaction with certain tetraorgano substituted ammonium salts, especially substituted ammonium bromides. Specifically the tetraorgano substituted ammonium salts must be those salts which are soluble in water and are capable of combining with molecular bromine to form a substantially water immiscible liquid complex.

Accordingly, in one aspect of the present invention there is provided an electrochemical cell comprising a metal anode having as its active component either zinc or cadmium; a bromine cathode; an aqueous metal bromide solution as electrolyte, the metal of the metal bromide being the same as the metal of the anode; and, as the sole bromine complexing agent, a water soluble tetraorgano substituted ammonium salt which combines with cathodic bromine to form a substantially water insoluble liquid complex, whereby shelf life and cell capacity are improved.

In another aspect of the present invention, there is provided an aqueous metal bromine secondary battery including a plurality of electrochemical cells, said cells comprising a metal anode having as active component zinc or cadmium; a nonreactive electrode; an aqueous electrolyte containing a metal bromide, the metal being the same as the metal of the anode; and, as the sole bromine complexing agent, a tetraorgano substituted ammonium bromide which is soluble in water, which forms a substantially water insoluble liquid complex with bromine and which acts as a source of cathodic bromine during cell discharge.

These and other embodiments of the present invention will become more apparent upon a reading of the detailed description in conjunction with the accompanying drawing, being a cross-sectional view of a cell in accordance with the present invention.

Turning now to the figure, there is shown one embodiment of the cell of the present invention. As illustrated in the figure an electrochemical cell of the present invention comprises a metal anode 10 disposed in a container 12 containing aqueous electrolyte 14.

The metal anode in accordance with the present invention is selected from zinc and cadmium. It should be noted, however, that it is not absolutely essential that the metal anode be formed solely of zinc or cadmium. Indeed, inert wire mesh or various forms of porous carbon materials upon which zinc or cadmium may be plated can serve very well in forming zinc or cadmium electrode.

Spaced apart from the anode 10 is a chemically inert electrode 16. Inert electrode 16 is disposed within container 12 so as to be in contact with aqueous electrolyte 14 and the bromine active cathodic material which material will be described hereinafter in greater detail. Turning first, however, to electrode 16 it should be noted that a wide range of inert materials can be used for fabricating

electrode 16, such as various forms of electrically conductive and non-corrosive materials, including porous carbon, graphite and carbon felt. Indeed, the inert electrode 16 preferably is formed of a highly porous material which will absorb the bromine active material. A suitable chemically inert electrically conductive material for forming an inert electrode 16 for the practice of the present invention is carbon felt, such as UCAR grade VDF carbon felt sold by Union Carbide Corporation, Carbon Products Division, 270 Park Avenue, New York, New York.

The electrolyte of the cell of the present invention is an aqueous metal bromide solution in which the metal of the bromide corresponds to the metal of the anode. Thus, when zinc is the anode active material the metal bromide used in the electrolyte is a zinc bromide. Similarly, with cadmium as the active metal anode material, the electrolyte is an aqueous cadmium bromide solution.

The concentration of metal bromide in the aqueous electrolyte is not critical and a wide range of concentrations may be employed depending, for example, on the desired energy density of the cell. Typically the molarity of the aqueous metal bromide solution will be in the range of about 2.5 to 3.5 molar although the concentration can be as low as 0.5 molar and as high as 6.0 molar and higher.

Optionally, and preferably, other salts such as zinc sulfate may be added to the electrolyte to improve electrolyte conductivity and/or zinc plating characteristics. The effects of such additives are well known and form no part of the present invention.

As is shown in the figure, the cell is provided with a separator 18 which prevents internal shorting that can typically occur as a result of dendrite growth. The separator 18 can be any porous material typically used to prevent physical contact of the two electrodes such as fiberglass mats, fiberglass felt, microporous polymeric materials such as porous polyethylene, and the like.

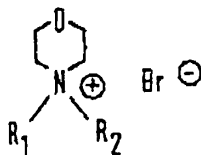
As is indicated hereinbefore, the cathode active material of the present invention is molecular bromine.

Additionally, the cathode active material is present as a substantially water insoluble liquid halogen complex of a tetraorgano substituted ammonium salt. The tetraorgano substituted ammonium salts suitable in the practice of the present invention are defined by the following characteristics. First, the tetraorgano substituted ammonium salt must be water soluble; and second, it must be one which is capable of combining with the cathodic bromine. Third, the halogen complex must be a substantially water immiscible liquid over a temperature range of from about 10°C. to about 60°C. and at least between 13°C. to 30°C. Preferred water soluble tetraorgano substituted ammonium salts can be represented by the general structural formula:



where the dangling valences of the nitrogen atom are connected to carbon atoms of saturated hydrocarbyl radicals forming a five-membered ring system including the nitrogen, or a six-membered ring system including another heteroatom. Typically, the other heteroatom will be oxygen or sulfur. In the above formula, R_1 is an alkyl or haloalkyl radical attached to the nitrogen atom by a carbon atom and R_2 is a different alkyl or haloalkyl organic radical attached to the nitrogen atom by a carbon atom. The anion of the salt, X^- , is a chloride or bromide anion and preferably is a bromide.

Preferably also, the tetraorgano radical substituted ammonium salt of the present invention is one in which the nitrogen atom is part of a said six-membered ring system including another heteroatom. Particularly preferred halogen complexes of the present invention are unsymmetrical morpholinium bromides represented by the formula:



wherein R_1 is a methyl group and R_2 is selected from alkyl groups having from 2 to

8 carbon atoms, such as ethyl, propyl, isopropyl and the like and haloalkyl groups having from 1 to 8 carbon atoms such as chloromethyl and bromomethyl groups.

The tetraorgano radical substituted ammonium salt used in the cell of the present invention is dissolved in the electrolyte solution 14 where it is available to complex the bromine upon charging of the cell. The amount of tetraorgano radical substituted ammonium salt used, e.g. the bromide, will depend upon the amount of metal bromide present and the depth of charge among other things. Generally, however, the ratio of tetraorgano substituted ammonium salt to metal bromide employed will be from about 1:4 to about 1:1. Typically, the ratio of tetraorgano substituted ammonium salt to metal bromide used will be 1:3.

The above-mentioned tetraorgano substituted ammonium salts are prepared by well known techniques. Typically these compounds are prepared by reacting an appropriate tertiary amine with an appropriate alkyl halide. For example, N-methyl, N-ethyl morpholinium bromide can be prepared by reacting N-methylmorpholine with ethyl bromide in a suitable solvent.

As will be appreciated, when the cell is charged bromine is produced at the surface of the inert cathode 16 where it will complex with the halogen complexing ammonium salt present in the electrolyte to form a liquid immiscible bromine complex. Thus, with a zinc bromide electrolyte bromine is generated at electrode 16 during charging of the cell. The bromine so generated is complexed by the ammonium salt while the zinc is deposited on electrode 10.

In the cell shown in the figure, it should be noted that the inert electrode 16 is a porous material which is capable of storing the liquid bromine complex within the pores of the electrode structure.

It will be appreciated that one of the advantages in the use of unsymmetrical (i.e., not having an axis of symmetry in the molecule) tetraorgano substituted ammonium salts in accordance with the present invention is that the bromine complex which results from the combination of the cathodic bromine and the salt is a liquid at least at cell operating temperatures and it is fluid. It does not require additional volumes of material such as aprotic solvents or organic materials to keep the complex in a liquid form thereby increasing the volume of the liquid that must be handled in order to complex the bromine.

The following examples illustrate modes of practicing the present invention.

EXAMPLE 1

A zinc-bromine secondary cell was constructed in which one electrode was formed from carbon powder and a plastic binder. The carbon and plastic binder was compressed on a tantalum screen current collector and used as an anode substrate for zinc deposition. A commercially available carbon felt material was impressed on a tantalum screen and used as an inert counterelectrode. Both electrodes had an area of 20 cm². Two layers of glass fiber filter paper was used as the battery separator. The assembly was then filled with an aqueous electrolyte containing 3 molar zinc bromide, 0.2 molar zinc sulfate and 1 molar N-methyl, N-ethyl morpholinium bromide. The theoretical capacity of the cell was 0.88 amp-hrs., based on zinc bromide.

The cell so constructed was cycled under a 0.19 amp charge and a 0.38 amp discharge regime, corresponding to current densities of 10 mA/cm² during charging and 20 mA/cm² during discharging. As is shown in Table I, the coulombic efficiencies are greater than or equal to 75% at the high material utilization in cycles 3 and 4.

TABLE I

Cycle	I ^c , A	Q ^c , A . hr	I ^d , A discharge	Q ^d , A . hr discharge	E, %
1	0.19	0.11	0.38	0.08	73
2	0.19	0.16	0.38	0.14	88
3	0.19	0.87	0.38	0.65	75
4	0.19	0.79	0.38	0.62	78

- (a) I^c is the current in the charging mode
 (b) Q^c is coulombs in the charging mode
 (c) I^d is the current in the discharging mode
 (d) Q^d is coulombs in the discharging mode
 (e) E is the efficiency

EXAMPLE 2

In this example the anode employed consisted of carbon powder in a plastic binder impressed on a tantalum screen. The inert counterelectrode consisted of a mixture of charcoal and carbon black in a tetrafluoro ethylene binder and impressed on a tantalum screen. A commercially available silica filled porous polyethylene sheet material was used as the battery separator. As in Example 1, the area of each electrode was 20 cm². The cell was filled with 7.0 cm³ of an aqueous electrolyte containing 3 molar ZnBr₂; 1 molar N-methyl, N-ethyl morpholinium bromide; and, 0.2 molar ZnSO₄. The theoretical capacity of the cell was 1.12 A . hr. The cell was put through a charging-discharging regime as shown in Table II below.

TABLE II

Cycle	I ^c , A	Q ^c , A . hr	%U	I ^d , A	Q ^d , A . hr	E, %
3	0.20	0.84	75	0.1	0.57	68
4	0.20	0.93	83	0.1	0.60	64
5	0.20	0.90	80	0.4	0.47	52
8	0.20	0.82	73	0.1	0.43	52

- (a) I^c is current in charging mode
 (b) Q^c is coulombs in charging mode
 (c) %U is percent utilization.

$$\%U = \frac{Q^c}{1.12} \times 100$$

- (d) I^d is current in discharging mode
 (e) Q^d is coulombs in discharging mode
 (f) E is cell efficiency

EXAMPLE 3

A comparative test was conducted using the cell of Example 2. In this test, however, 6.0 cm³ of aqueous electrolyte was employed and the electrolyte did not contain any halogen complexing ammonium salt. The electrolyte merely contained 3 molar ZnBr₂ and 0.2 molar ZnSO₄. The theoretical capacity of this cell was 0.96 A . hr. The cycling regime and the results thereof are given in Table III below.

TABLE III

Cycle	I ^c , A	Q ^c , A . hr	%U	I ^d , A	Q ^d , A . hr	E, %
2	0.2	0.77	80	0.4	0.31	41
4	0.2	0.64	67	0.4	0.20	31
5*	0.2	0.45	47	0.1	0.0	0
6	0.2	0.86	90	0.1	0.26	30
8	0.2	0.86	90	0.1	0.30	35

- (5*) The cell was allowed to stand at open circuit potential between charge and discharge for 15 hours

- (a) I^c is current during charging mode
 (b) Q^c is coulombs in charging mode
 (c)

$$\%U = \frac{Q^c}{0.96} \times 100 = \text{percent utilization}$$

- (d) I^d is current during discharging mode
 (e) Q^d is coulombs in discharging mode
 (f) E is cell efficiency

As can be seen in this example, the cell is less efficient than the cell of this invention and is also subject to self discharge.

In our copending application 10,159/77 (Serial No. 1568398) we describe and claim an electrochemical cell having a metal bromine couple comprising:

an electrode structure on which to deposit the metal of the metal bromine couple;

an inert counterelectrode structure at which to generate the bromine of the metal bromine couple;

an aqueous electrolyte containing a metal bromide and a bromine complexing agent, the metal of said metal bromide being selected from zinc and cadmium, said bromine complexing agent being defined as one or more compounds selected from water-soluble organic quaternary ammonium compounds or mixtures thereof with water soluble organic solvents, and which in the presence of bromine and at temperatures in the range 10° to 60°C form a substantially water-immiscible liquid;

means for circulating said electrolyte between said electrode structures during charging of the cell;

a separation zone communicating with said cell, whereby bromine complex formed during charging of the cell is separated from said aqueous electrolyte; and

means for circulating separated bromine complex from said separation zone to said cell during discharge of said cell.

In our copending application 12,622/77 (Serial No. 1569399) we describe and claim an electrochemical cell comprising: a metal anode having as its active component either zinc or cadmium; a bromine cathode; an aqueous electrolyte containing a metal bromide, the metal bromide having the same metal as the metal of the anode; and, as the sole bromine complexing agent, a quaternary ammonium salt of an N-organo substituted alpha amino acid, which quaternary ammonium salt is soluble in water and forms a substantially water immiscible liquid bromine complex.

WHAT WE CLAIM IS:—

1. An electrochemical cell comprising: a metal anode having as its active component either zinc or cadmium; a bromine cathode; an aqueous electrolyte containing a metal bromide, the metal bromide having the same metal as the metal of the anode; and, as the sole bromine complexing agent, a tetraorgano substituted ammonium salt which salt is soluble in water and forms a substantially water immiscible, liquid, bromine complex.

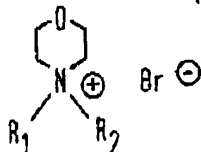
2. A cell as claimed in claim 1 wherein the water soluble tetraorgano substituted ammonium salt has the formula:



wherein (a) the dangling valences of the nitrogen atom indicate that the nitrogen is a heterocyclic nitrogen atom connected to carbon atoms to form either a saturated five-member ring structure or a saturated six-member ring structure, which latter includes an additional heteroatom, (b) X^- is chloride or bromide, and (c) R_1 is selected from alkyl groups and haloalkyl groups of from 1 to 8 carbon atoms and R_2 is selected from different alkyl groups or haloalkyl groups of from 1 to 8 carbon atoms than R_1 .

3. A cell as claimed in claim 2, wherein the halide, X^- , is bromide.

4. The cell as claimed in claim 3, wherein the tetraorgano substituted ammonium salt is a morpholinium bromide having the formula:



wherein R_1 is a methyl group and wherein R_2 is an alkyl group having from 2 to 8 carbon atoms or is a chloromethyl group.

5. A cell as claimed in claim 4, wherein the quaternary ammonium salt is N-methyl, N-ethyl morpholinium bromide.

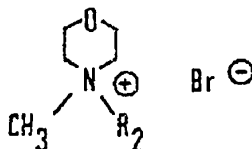
6. A cell as claimed in any one of claims 2 to 5, wherein the anode is zinc and the electrolyte is an aqueous zinc bromide solution.

7. An aqueous metal-halogen secondary battery including a plurality of electrochemical cells, said electrochemical cells comprising: a metal anode having as its active component zinc or cadmium; an inert counterelectrode; an aqueous electrolyte, said aqueous electrolyte consisting of an aqueous metal bromide solution in which the metal is the same as the metal of the anode; and, a cathodically active bromine complex which is a liquid and substantially water immiscible, said bromine complex being formed solely between bromine and a water soluble tetraorgano substituted ammonium bromide having the general formula:

Br[⊖]

wherein the dangling valences of the nitrogen atom indicate that nitrogen is a heterocyclic structure selected from saturated five membered structures and saturated six-membered structures containing only carbon and hydrogen and another heteroatom and wherein R₁ is selected from alkyl groups having from 1 to 8 carbon atoms and R₂ is selected from alkyl groups and halosubstituted alkyl groups having from 1 to 8 carbon atoms but different from R₁.

8. A battery as claimed in claim 7, wherein the metal anode is zinc and wherein the aqueous electrolyte is a solution of zinc bromide and wherein the quaternary ammonium compound is an unsymmetrical morpholinium compound having the general formula:



wherein R₂ is an alkyl radical having from 2 to 8 carbon atoms or a chloromethyl group.

9. An aqueous metal-halogen, secondary battery including a plurality of the electrochemical cells defined in claim 1.

10. An electrochemical cell as claimed in claim 1 and substantially as herein described.

11. An electrochemical cell as claimed in claim 1 and substantially as described in Example 1 or Example 2 herein.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

